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SPS of "Titanium Carbide/Carbohydride – Copper" Composites

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Abstract

The TiC-copper and $Ti_2CH_{0.6}$-TiC-intermetallic Cu-Ti composites were produced using high-energy wet ball milling of Ti-Cu-graphite and Ti-Cu-surfactant powders, respectively, followed by spark plasma sintering at 900°C. The composites were shown to be of 91-92% in density as compared with the theoretical value, microhardness of 6-7 GPa, and elasticity modulus of 134-140 GPa. The tribological properties of the composites were shown to depend on the phase composition. Surfactant addition resulted in higher fretting resistance against tempered steel (C-1%, Cr-1.5%) due to the formation of hexagonal titanium carbohydride and higher abrasive wear resistance.

Keywords: titanium carbide; titanium carbohydride, composite; ball milling; spark plasma sintering

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1. Introduction

Wide application of hard composite materials in modern technologies stimulates a search for new compositions as well as more efficient and cheaper ways of their obtaining and improved operational characteristics. Traditionally, tungsten-carbide-based hard alloys with cobalt binder provide the most advantageous properties, but they are quite expensive. In addition, cobalt is toxic. Currently, much attention is paid to titanium carbide composites. To improve the properties of titanium carbide alloys, new binder compositions are being developed. The carbide and binder phases are transformed into a nanostructured state, and various additives being added to reduce the carbide phase grain size and improve the adhesion between the carbide grain and binder phase. Mechanochemical synthesis is an effective way of obtaining powdered titanium carbide. To reduce contamination by the milling equipment material, the milling process is carried out in the presence of liquid hydrocarbons. Using liquid hydrocarbons as a milling medium and as a carbon source allows one to obtain carbide powders with a small particles size. Under milling in liquid hydrocarbons, the formation of titanium

carbide proceeds through an intermediate stage of the formation of carbohydrides, as described in Ref. [1-3]. To accelerate the processes of the carbide formation, additional sources of carbon (graphite, carbon black, etc.), as well as surfactants, may be added into the mixtures of powdered titanium and binder, which facilitate faster milling process of initial powders and formation of high specific surface.

In this work, we compared the structural-phase state and properties (density, microhardness, fretting resistance, abrasive wear resistance) of titanium carbide and titanium carbohydride - copper composites obtained by high-energy ball milling of Ti + 10 vol% Cu powders with graphite or octadecylamine (ODA) additions in petroleum ether followed by spark plasma sintering (SPS). ODA accelerates carbide formation under mechanical activation [4] and completely decomposes at temperatures above 400°C.

2. Experimental Procedures

Two types of samples were studied: a mixture of powders of 66 wt% titanium, 17 wt% copper and 17 wt% graphite was taken for sample 1, for sample 2 - 66 wt% titanium, 17 wt% copper and 3 wt% ODA. The powder samples were prepared by high-energy ball milling of the initial powders of Ti (99.0 wt% purity and particle size ~40 μm), Cu (99.7 wt%, ~18 μm), graphite (99.9 wt%, ~1000 μm) and ODA (97.0 wt%) using a Fritsch P-7 planetary ball mill. Ten grams of powders were charged in a steel (1 wt% C, 1.5 wt% Cr) milling vial with grinding balls. The weight ratio of balls to powders was about 8 to 1. The milling vials were filled with petroleum ether (analytical grade) as a milling medium and a carbon source. To prepare the powder sample 1 titanium-copper powder mixture was premilled during 1 h, then graphite powder was added and powder mixture milled for 3 h. In the case of powder sample 2 three-stage milling was used: at the first stage titanium powder was milled for 4 h, at the second stage ODA was added and powder mixture milled for 0.5 h, and at the third stage copper powder was added and powder mixture milled for 0.5 h yet.

To prepare the samples for spark plasma sintering the milled powders were preliminary compacted via hand-operated hydraulic press with graphite dies at max load of 5 kN. Pressed intermediates were further sintered in HP D25 (FCT System GmbH, Germany) at the temperature 900°C and the pressure 24 MPa for 1 minute in vacuum 10^{-1} Pa (pulse duration was 5 ms, 4.6 V constant voltage and 1 kA current). The diameter and height of the prepared samples were 20 mm and ~1 mm correspondingly.

Structural and phase state was characterized by X-ray diffraction on MiniFlex (Rigaku) using Co Kα radiation. Composite microstructure and component distribution were

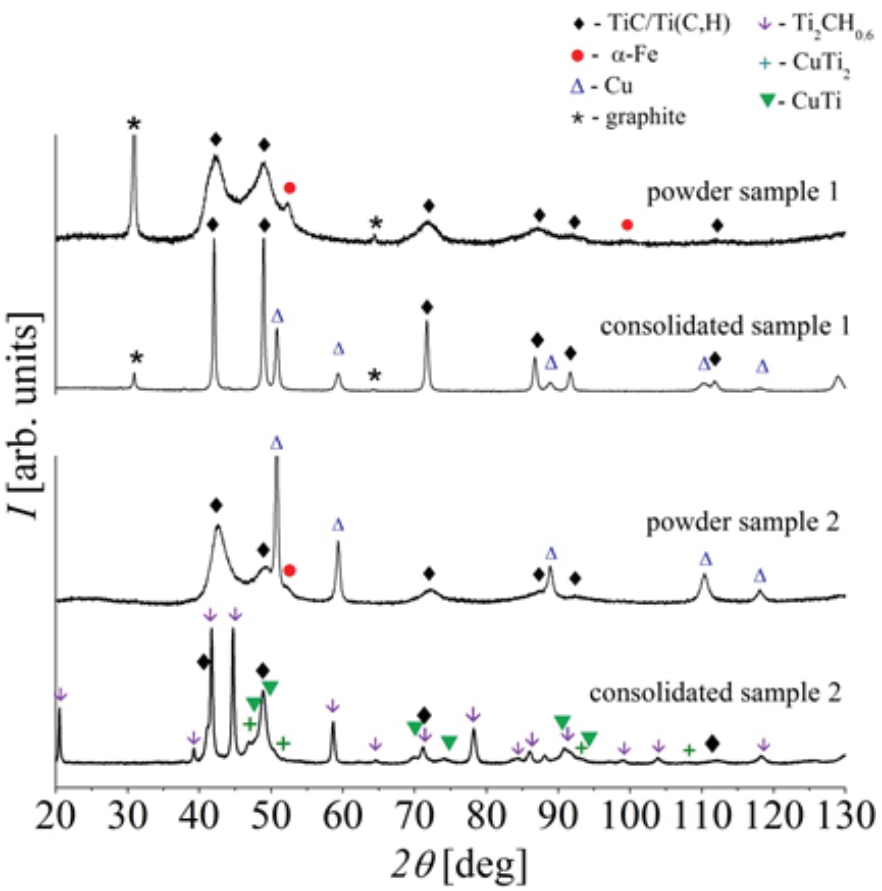

Figure 1: XRD patterns of powders and consolidated samples 1 and 2.

examined by a scanning electron microscopy (SEM) on JEOL JSM-6490LV. Density of samples was measured using hydrostatic technique. Vickers microhardness measurements were carried out ten times for each sample on PMT-3 machine with 0.98 N load. The elastic modulus curves were obtained using the Micro-indentation Tester (CSM Instruments) with a 9 N load using the Oliver-Pharr method [5]. Fretting wear resistance were examined on SRV–III Test System (Germany) using vibration module and reciprocating motion against 9.4 mm tempered carbon steel ball (hardness 55–57 HRC, roughness R_a = 0.02) at room temperature and 30% ambient humidity for 20 minutes. The load was constant and equal to 10 N. Displacement of the steel ball was 2 mm; the vibration frequency was 20 Hz. Abrasive wear resistance against corundum abrasive cloth KK19XW with three different grain sizes M40 (28–40 μm), 5-H (50–63 μm) and 40-H (400–500 μm) was estimated using the technique described in Ref. [6]. Wear rates were measured on VLA-200g-M analytic balance as an average of three measurements. Measured values were normalized by sample surface areas. Inaccuracy of mass measurements was ±2 mg.

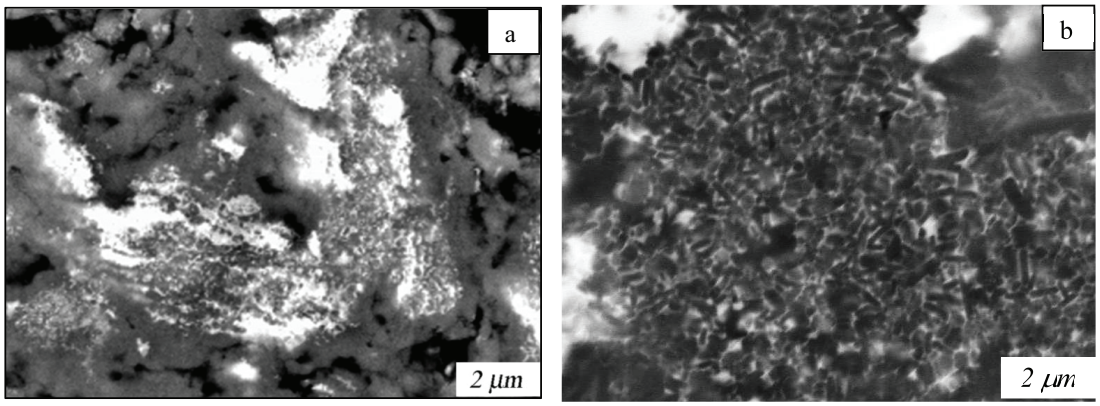

Figure 2: SEM images of consolidated samples (a) 1 and (b) 2.

3. Results and Discussion

TABLE 1: The properties of the consolidated samples.

Sample	Phase composition [wt%] (±5)	Density [g·cc^{-1}] (±0.05)	HV [GPa]	Modulus of elasticity [GPa]	Max friction coefficient (±0.01)	Normalized abrasive wear against emery cloth [mg·mm^{-2}] (±0.002)		
						M40	5-H	40-H
1	TiC –76 Cu – 16 C_{gr} – 8	4.3	7.2±1.2	133±3	0.83	0.041	0.083	0.296
2	$Ti_2CH_{0.6}$ – 44 TiC – 28 CuTi – 22 $CuTi_2$ – 6	4.9	6.3±0.6	140±4	0.41	0.031	0.055	0.154

X-ray diffraction patterns of the samples are shown in Fig. 1. Mechanical activation led to the formation of supersaturated solid solution of hydrogen and carbon in titanium. Broad peaks in XRD patterns of the both powder samples correspond to the FCC solid solution of H and C in Ti. In the case of sample 1, there are no any visible peaks of FCC copper. Copper-containing phase is observed as highly dispersed intermetallic compounds with titanium or Cu-Ti amorphous phase [6]. Sample 2 contains ~17 wt% of FCC copper phase because of milling conditions.

The phase composition analysis of the consolidated samples shows that an addition of graphite has a significant effect on its final phase composition (Fig. 1). The presence of graphite in sample 1 leads to the formation of titanium carbide and copper phases in sintered specimens. For sample 2 obtained by mechanical activation with added ODA, but without graphite, the hexagonal titanium carbohydride of $Ti_2CH_{0.6}$ type is predominant in the phase composition. The titanium carbide and intermetallic phases are also

present. The difference in the phase compositions of consolidated samples are due to different percentage of carbon needed for the formation of titanium carbide. In the case of sample 1, carbon amount was enough to form titanium carbide. The lattice parameter of titanium carbide was found to be 0.4322(1) nm which is close to stoichiometric value (0.4328 nm). Intermetallic titanium-copper phases were not formed, since the formation of titanium carbide is thermodynamically more favorable. Sample 2 is characterized by carbon deficiency, resulting in the formation of the hexagonal titanium carbohydride.

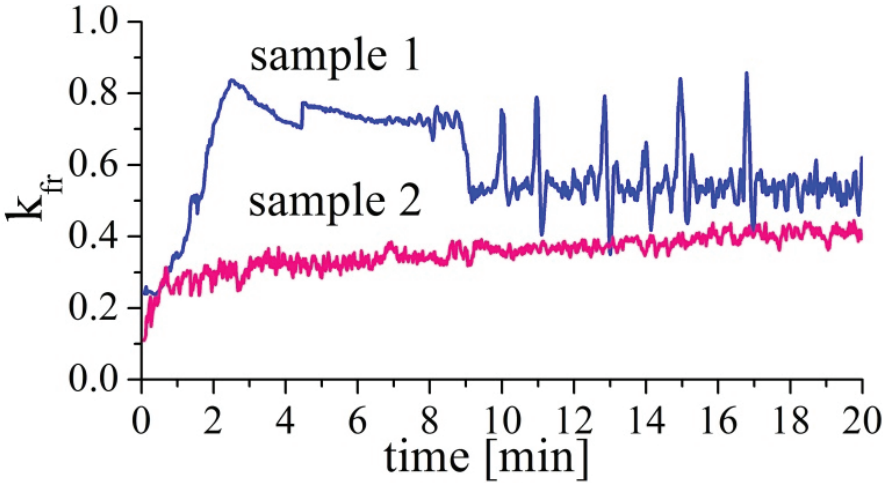

Figure 3: Friction coefficient vs time for the consolidated samples 1 and 2.

Based on the analysis of SEM image shown in Fig. 2, it can be concluded that the structure of sample 1 is consisted of the titanium carbide coarse grains, graphite inclusions, as well as the regions without clear boundaries and having a eutectic-like structure. One of these “eutectic” phases is copper (or solid solution of titanium in copper), and another being titanium carbide. SEM image of sample 2 shows interlayers of intermetallic phase seen as light areas and dark plates or disks of titanium carbohydride and titanium carbides. The diameter of the latter does not exceed 1 μm, with the thickness being up to 300 nm.

The properties of the composites are summarized in Table 1. The density of the samples is 91-92% of theoretical values. Although 76 wt% of consolidated sample 1 was stoichiometric titanium carbide, which has potential of 32 GPa, its microhardness was only 7 GPa. It may be explained by the small grain size of the carbide phase distributed in the soft matrix, by the porosity and graphite presence. The lower abrasive wear resistance also could be associated with the presence of graphite inclusions. The maximum friction coefficient of the ”sample 1-counterbody” pair was 0.8 (Fig. 3). It was shown, that the surface of sample 1 after 20 minutes of fretting wear was practically unworn due to the formation of thick graphite and iron oxide lubricant film. Sample 2 demonstrated lower

friction coefficient due to lamellar structure of the hexagonal carbohydride and higher abrasive wear resistance.

4. Conclusion

The ”titanium carbide - copper” and ”titanium carbohydride/carbide – intermetallic $CuTi_2$, CuTi” composites with a density of 91-92% of the theoretical value were produced by high-energy ball milling of Ti-Cu-graphite and Ti-Cu-surfactant (octadecylamine) powders in liquid hydrocarbon (petroleum ether) and followed by spark plasma sintering at 900°C. Mechanosynthesis of powders without graphite followed by spark plasma sintering made it possible to obtain consolidated samples with a microhardness of 6 GPa, an elastic modulus of 140 GPa, better fretting parameters and higher abrasive wear resistance than that of samples based on titanium carbide, copper and dispersed graphite phase.

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